SYMPOSIUM ON GEOCHEMISTRY AND CHEMISTRY OF OIL SHALE
PRESENTED BEFORE THE DIVISIONS OF FUEL CHEMISTRY, GEOCHEMISTRY
AND PETROLEUM CHEMISTRY, INC.
AMERICAN CHEMICAL SOCIETY
SEATTLE MEETING, MARCH 20-25, 1983

GEOCHEMISTRY OF ISRAELI OIL SHALES - A REVIEW

By

M. Shirav (Schwartz) and D. Ginzburg
Geological Survey of Israel, 30 Malkhe Yisrael St., Jerusalem 95501, Israel

INTRODUCTION

The oil shales in Israel are widely distributed throughout the country (Figure 1). Outcrops are rare and the information is based on boreholes data. The oil shale sequence is of Upper-Campanian - Maastrichtian age and belongs to the Chareb Formation (Figure 2). In places, part of the phosphorite layer below the oil shales (Mishash Formation, Figure 2) is also rich in kerogen. The host rocks are biomicritic limestones and marls, in which the organic matter is generally homogeneously and finely dispersed. The occurrence of authigenic feldspar and the preservation of the organic matter (up to 26% of the total rock) indicate euxinic hypersaline conditions which prevailed in the relative closed basins of deposition during the Maastrichtian (1).

Current reserves of oil shales in Israel are about 3,500 million tons (2, 3), located in the following deposits (Figure 1): Zin, Oron, Ef'e, Hartuv and Nabi-Musa. The 'En Bokek deposit, although thoroughly investigated, is of limited reserves and is not considered for future exploitation. Other potential areas, in the Northern Negev and along the Coastal Plain are under investigation.

Future successful utilization of the Israeli oil shales, either by fluidizid-bed combustion or by retorting will contribute to the state's energy balance.

CHEMISTRY

Typical analyses of Israeli oil shales are shown in Table I.

TABLE I

CHEMICAL ANALYSES OF OIL SHALE SAMPLES (WT %)

	Ef'e Bor. 1	Ef'e Bor. 1	Hartuv Bor. HRB	Hartuv Bor. HRB
	18-22m	60-70m	62-82m	130-150
SiO_2	16.9	7.6	7.5	5.0
Al_2O_3	6.8	1.5	1.61	1.32
TiO_2	0.32	0.16	0.1	0.1
Fe_2O_3	2.8	0.7	1.01	0.57
CaO	34.2	36.1	37.7	38.2
MgO	0.57	0.58	1.67	0.39
Na_2O	0.27	0.20	0.14	0.10
K_2O	0.42	0.32	0.15	0.14
P_2O_5	1.6	3.5	3.0	2.3
SO_3	2.3	0.9	0.3	0.26
S (Org)	1.4	2.7	1.7	2.4
Org. Mat.	8.2	24.1	14.8	20.5
L.O.I	33.5	45.7	44.0	49.6

One borehole in the Ef'e deposit, T1, coord. 1167/0544 (Israel Grid) was analyzed meter by meter; the correlation factors between the variables are summed up in Figure 3.

SiO_2 content is 2-14 wt %. The significant correlation with Al_2O_3 and Fe_2O_3 indicate its residence in clay minerals. Free silica, in the form of quartz grains is rare.

CaO (30-40 wt %) constitutes calcite (50-70% of the total rock). Little amounts of CaO are located in apatite and gypsum.

Al_2O_3 is a main component in clay minerals. Al_2O_3 is highly correlative with SiO_2, Fe_2O_3 and TiO_2. The content of Al_2O_3 along the oil shale sequence is 1-7 wt %.

Fe_2O_3 content is 0.5-2 wt % and it is located in clay minerals and pyrite.

Sulfur is shown on Figure 3 as SO_3, which includes organic and inorganic sulfur. Direct observations and isotopic composition of sulfur (4) indicate that kerogen-bound sulfur accounts for 60-80% of the total sulfur in the rock while the remainder is pyritic and gypsum sulfur.

P_2O_5 content within the oil shale is 1-5 wt %, while in the phosphorous Mishash Formation it may exceed 30%.

Organic matter (kerogen) composes 5-26 wt % of the rock. The average content of organic matter in Israeli deposits is 14-16 wt %. Only rocks with more than 10% organic matter, are considered as "economic" oil shales.

Depth shows significant positive correlation with the following variables: organic matter, SO_3, P_2O_5 and negative correlation with Al_2O_3, Fe_2O_3 and SiO_2. As Al, Si and Fe are dependent upon clay content, it is clear that the amount of clay decreases with depth. Organic matter, SO_3 (the part included in organic matter and in gypsum) and P_2O_5 contents increase with depth. Thus, these data represent a mineralogical system of four main variables, changing with geological time (=depth) (Figure 2). The 4 main mineralogical phases are: carbonate, clay minerals (mainly montmorillonite and kaolinite), apatite and organic matter. Other minor constituents are pyrite, gypsum, quartz and feldspar. This system is one clue to the understanding of the paleogeographical set-up during the Maastrichtian in Israel, as well as a main factor for any assessment of oil shale's quality.

Effect of $CaCO_3$ on Combustion

Fluidized bed technology seems to be preferable for oil shale combustion (5). Series of combustion tests which were run in different temperatures resulted in lower effective calorific value with the increase of operating temperature. Figure 4 shows a DTA curve for a typical Israeli shale. When operating the fluidized bed in the range of 700-800 °C endothermic reactions are only in their beginning, but if the operating temperature exceeds 800-850°C, the endothermic reaction of calcite decomposition has a severe influence on the effective calorific value. Fluidized beds burning coal use a certain amount of carbonate for SO_3 trapping, but in this case more than 60% of the material which is fed to the burner is carbonate. Thus, the necessity of maintaining delicately-controlled conditions during combustion is a direct outcome of the inorganic composition of the oil shale.

CALORIFIC VALUE

The high calorific value of the oil shale was determined by a "bomb" calorimeter on more than 50 composite samples from different deposits and on one-meter samples along borehole sections. The average value is 1000Kcal/Kg and the highest value measured was 1790Kcal/Kg. The correlation between organic matter content to the high calorific value is more than significant (R=0.96). The equation for the Ef'e deposit is:

a) calorific value = 77.8 + 60.2 (org. matter wt %)

and for the Hartuv deposit

b) calorific value = 52.0 + 71.3 (org. matter wt %)

The line for the Hartuv deposit is steeper than that for the Ef'e deposit (Figure 5) i.e.: in the range of 14 wt % organic matter (average for most of the deposits) the difference will be 120Kcal/Kg in favor of the Hartuv deposit. As the overall inorganic composition is similar in the two deposits, we assume that the reason for this difference is due to compositional variations within the organic matter.

FISCHER ASSAY

Fischer assay tests were carried out on several boreholes in the Ef'e deposit (6). The average yield was 15.6 Gal/Ton; sections with high content of organic matter (20-26 wt %) yielded up to 29 Gal/Ton. Evidently, there is a positive correlation between Fischer assay and the content of organic matter; another interesting relation is illustrated in Figure 6. With the increase of depth, more oil is yielded per wt % of organic matter. The data in Table II suggest that this phenomenon may be related to changes in the elemental composition of the oil shale and/or to the content of bituminous fraction within the organic matter.

TABLE II

ULTIMATE ANALYSES AND OIL YIELD

Sample No.	Org. C %	H %	N %	S %	Oil, Gal/Ton	% Bitumen of TOM
SRV208	7.8	1.28	0.29	2.4	11.9	6.8
SRV215	10.1	1.56	0.35	3.0	16.5	7.1
SRV221	13.6	1.76	0.54	3.1	24.2	7.8

TOM = Total Organic Matter

The average composition of kerogen from the Ef'e deposit is:

C-64.9% H-8.0% N-2.8% S-9.1%

The average composition of retorted oil from the Ef'e deposit is:

C-79.8% H-10.1% N-1.1% S-7.6%

TRACE ELEMENTS

Table III summarizes trace elements concentration data in the oil shale sequence of the Ef'e deposit, the phosphorite layer from the same area (7) and the Green River oil shale (8).

TABLE III

TRACE ELEMENTS DATA (PPM)

	Ef'e 1	Ef'e 2	Phosphate	Green River
Ba	250	200	500	N.D.
Cr	430	450	200	49
Cu	95	100	25	15
Li	17	17	N.D.	850
Mn	30	35	40	34
Ni	125	135	70	11
Rb	10	5	4	29
V	70	75	170	29
Pb	17	35	N.D.	N.D.
Y	34	11	83	1.2
Zn	160	175	430	13
Zr	38	50	N.D.	9.3
U	20	40	150	1

N.D. = not determined

The Ef'e oil shale has higher concentrations of trace elements than the Green River oil shale (except for Li). Concentration of those elements which occur in apatite (7) - V, Zn, Y, U - are much higher in the phosphorite layers. Ni and Cu are correlative with the Fe_2O_3 content (not shown in the Table) suggesting their occurrence in association with pyrite or as an independent phase. Generally, there is not any evidence for an accumulation of trace elements as a result of high concentrations of organic matter.

SUMMARY

The Israeli oil shales may be considered as a multi-variable system, in which the main components influencing their quality are organic matter, carbonate, clay minerals and apatite. As

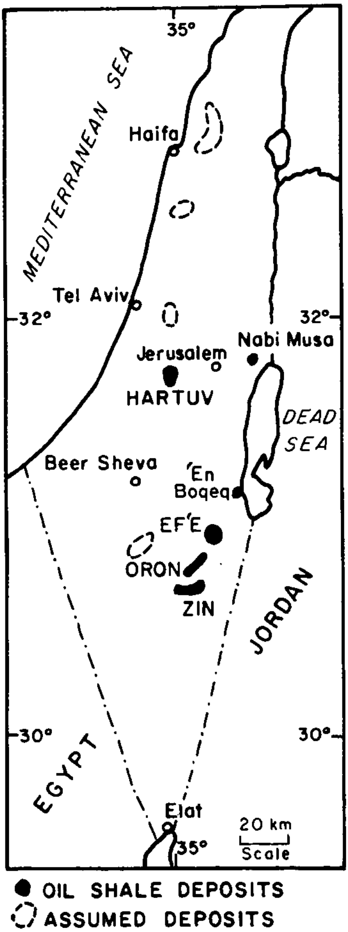

Figure 1. Location Map

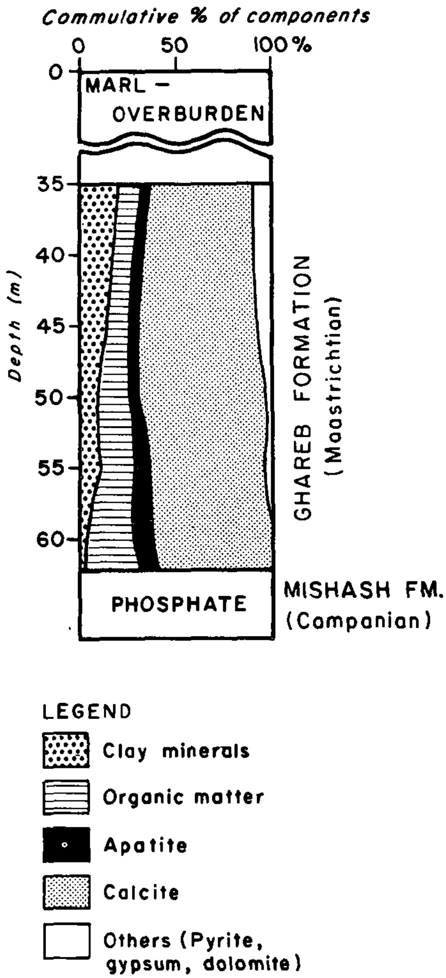

Figure 2. Mineralogical log (Bor. Ti)

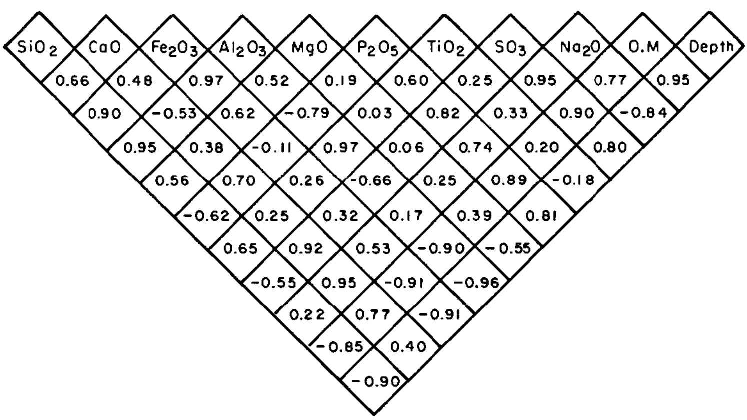

Figure 3. Correlation factors for chemical analyses of samples from Borehole T1, Ef'e deposit (O. M=Organic Matter)

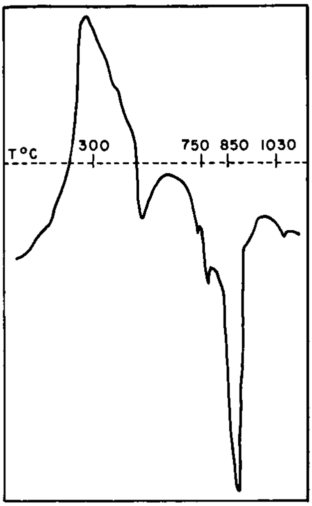

Figure 4. DTA curve for sample HRB-3a

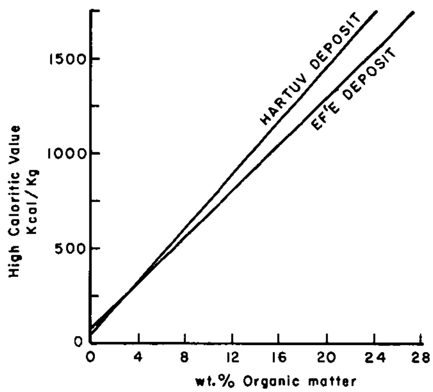

Figure 5. Correlation between organic matter content and high calorific value (Ef'e and Hartub deposits)

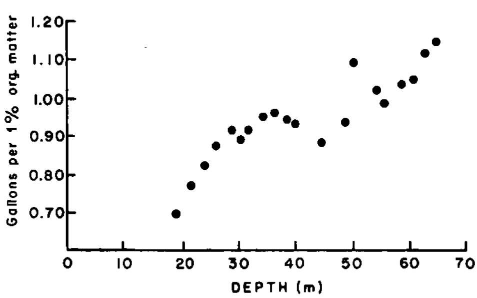

Figure 6. Oil yield per 1 wt % of organic matter as a function of depth (Borehole Bit1, Ef'e)

the percentage of these components varies over the vertical section, depth also plays a significant role whenever a quality assessment of the shale is done. Compositional variations within the organic matter are responsible for changes in the relative calorific value and retorted oil yield while fluidized bed combustion is affected by the inorganic components.

LITERATURE CITED

(1) Shirav (Schwartz), M. and Ginzburg, D., "Distribution and Depositional Environment of the Oil Shale Deposits in Israel", 10th Intl. Cong. on Sedimentology, Jerusalem, Israel. Abstracts Vol. II, pp. 601-602 (1978).

(2) Shirav (Schwartz), M. and Ginzburg, D., "A Guidebook to the Oil Shale Deposits in Israel", Int. Symp. on Oil Shale Chem. and Tech., Jerusalem, Israel, 32 pp. (1978).

(3) Shirav (Schwartz), M. and Ginzburg, D., A New Oil Shale Deposit in the Hartuv-Zora' Region, GSI Rep. No. MP 597/80, 15 pp. (1980).

(4) Dinur, D., Spiro, B. and Aizenshtat, Z., The Distribution and Isotopic Composition of Sulfur in Organic-Rich Sedimentary Rocks, Chem. Geol. 31, 11. 37-51 (1980).

(5) Wohlfarth, A., Dibner, I., Keren, Y. and Berkovitz, Y., Combustion of Oil Shale for Industrial Steam Production, Intl. Symp. on Oil Shale Chem. and Tech., Jerusalem, Israel, Abstract (1978).

(6) TOSCO Corp., Ef'e Oil Shale Deposit, Int. Rep. (1975).

(7) Nathan, Y., Shiloni, Y., Roded, R., Gal, I. and Deutch, Y., The Geochemistry of the Northern and Central Negev Phosphorite (Southern Israel), GSI Bull. No. 73, 41 pp. (1979).

(8) Cook, E. W., Elemental Abundances in Green River, Oil Shale Chem. Geol. 11, pp. 321-324 (1973).